

Preparation and Properties of Thermoplastic Starch-Polyester Laminate Sheets by Coextrusion

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The effects of extrusion and formulation variables on the structure and properties of starch-polyester laminates were examined. Three-layer polyester/starch/polyester sheets were prepared using a twin-screw extruder for the starch/water center layer, a single screw extruder for the outer polyester layers and a feedblock and coathanger type sheet die. Overall sheet and coating thicknesses were more uniform as coating polymer (poly(ϵ -caprolactone), PCL) viscosity decreased (lower molecular weight), starch melt viscosity increased (lower moisture) and feedblock/die temperature increased. Peel strengths were 1 to 2 orders of magnitude larger for high than low molecular weight PCL. High peel strengths were associated with rough, wavy interfaces (interfacial instability). Addition of plasticizer such as glycerol and sorbitol to the starch decreased peel strengths. Peel strengths varied little with type of polyester coating, except, perhaps, for polylactic acid and polyesteramide, which were more difficult to peel. Some possible applications of laminated starch sheets include food packaging and controlled release of drugs, pesticides, insect diets, etc.

INTRODUCTION

Starch is composed of amylose, a mostly linear polymer of α -1,4 linked glucose units, and amylopectin, a highly branched polymer of short, α -1,4 linked chains connected by α -1,6 linkages (1-5). Starch has received considerable attention recently as a possible alternative to petroleum based polymers for disposable packaging applications (6-9). It has the advantages of being inexpensive, renewable, produced in large amounts in the U.S., and biodegradable. Starch can be melt processed with water or other hydrophilic plasticizers in extruders in much the same way as conventional polymers (10-12). An inherent problem with the use of thermoplastic starch based polymers as biodegradable plastics is their sensitivity to water

(2). Thermoplastic starch will, after immersion in water, rapidly absorb moisture and lose most of its strength.

One approach toward solving this problem is to laminate thermoplastic starch with water-resistant, biodegradable polyesters. Of the different techniques for lamination, coextrusion would seem to be preferred since no solvents are used and the entire process is completed in a single step. Although coextrusion of starch-polymer laminates has been mentioned in the patent literature (13-15), there have been no detailed studies of the effects of composition and processing conditions on laminate structure and properties. In the present study, the effects of processing conditions, molecular weight and type of polyester and addition of plasticizer to starch on coating uniformity and peel strengths were examined.

EXPERIMENTAL

Materials

Corn starch (Buffalo 3401, 10.3% moisture) was purchased from CPC International, Englewood Cliffs, N.J. Poly(ϵ -caprolactones) (Tone P-767, Mw 40,000

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and Tone P-787, Mw 80,000) were purchased from Union Carbide, Danbury, Conn. Polybutylene succinate adipate (Bionolle 3001, Mw 100,000) was purchased from Showa Highpolymer, Tokyo, Japan. Polybutylene adipate/caprolactam (BAK 1095) was obtained from Bayer, Germany. Poly(lactic acid) (PLA, approximately 95% L) was obtained from Cargill Co., Minneapolis, (now Cargill/Dow Polymers, Minnetonka, Minn.). Polybutylene adipate terephthalate (Copolyester 14766) was obtained from Eastman Chemical Co., Kingsport, Tenn.

Preparation of Laminate Sheets

Laminate sheets were fabricated using a cast film line (Randcastle Extrusion Systems, Inc., Cedar Grove, NJ) with a 3-layer feedblock and a 6 inch flexible lip, coathanger die (die gap 1 mm). Outer (polyester) layers were formed using a Randcastle 1/2 inch diameter, 24/1 L/D single screw extruder. Screw speeds were varied from 5-20 rpm to change the thickness of the outer layers. The inner (starch) layer was formed using a Micro-18 30/1 L/D co-rotating twin screw extruder (American Leistritz Extruder Co., Somerville, N.J.). The screw configuration was:

30/90 20/30 15/60 10/30 KB30R/20
10/20 KB90/20 30/30 KB60R/20 20/20
KB60L/20 20/60 KB60R/20 20/20
KB60L/20 15/30 10/30

where the first number is the pitch and the second the length in mm except for kneading blocks (KB) where the first number indicates the angle between blocks. The barrel had six different zones, each 90 mm long, which were controlled to the following temperatures (°C):

#	zone 1	zone 2	zone 3	zone 4	zone 5	zone 6
1	20	45	130	130	130	130
2	20	45	150	150	150	150

The higher temperature settings were used for low moisture content starch (20%) while the lower temperatures were used for higher moisture starch (25–35%) (see **Results**). Feedblock and die temperatures were 115–145 and 80–110°C, respectively (see **Results**). Corn starch was fed into zone 1 at 50–60 g/min using an Accurate Model 106 volumetric feeder (Accurate, Whitewater, Wis.) or a K-tron Model KCL24 twin-screw gravimetric feeder (K-tron, Pitman, N.J.). Distilled water was pumped into zone 2 at rates calculated to give a starch-water mixture having 20–35% moisture using a high pressure piston pump (Eldex Labs, Napa, Calif.). Screw speeds were 3–400 rpm. Sheets were taken off with a Randcastle chill roll. Samples were equilibrated at 23°C and 50% humidity for 1 week and 12 weeks prior to testing.

Sample Analyses

Peel tests were performed with an Instron Universal Testing Machine Model 4201. Starch-polyester laminates were first cut into 100 × 25 mm pieces. Next, a 12.5 mm wide strip of the polyester coating was cut using a razor blade and an end of the polyester was peeled from the starch. This end was gripped with the upper grip of the crosshead while the starch sheet was held in a horizontal position on the base of the Instron. The polyester film was then pulled off the starch sheet at a rate of 50.8 mm/min. A special traveling base fixture was employed to keep a constant 90° angle between the polyester film and starch. Results presented are the average of tests of 4–8 specimens.

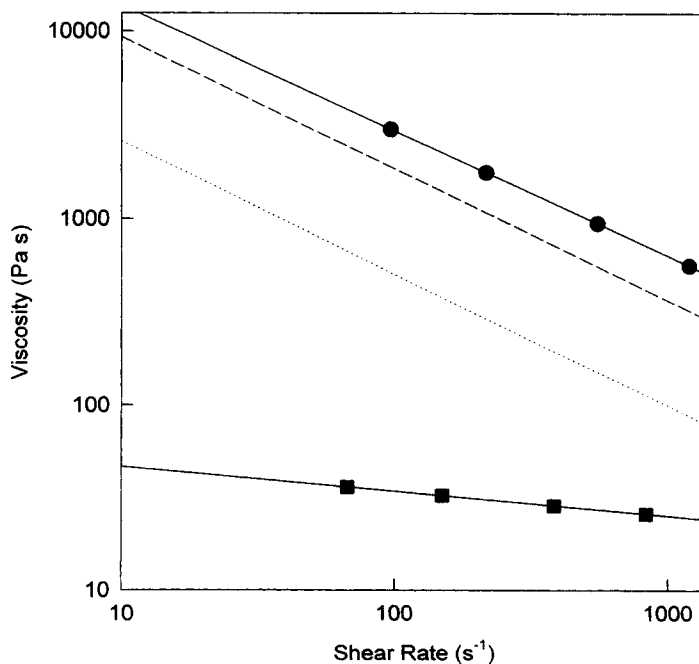


Fig. 1. Melt viscosities of PCL 767 (■), PCL 787 (●), starch with 35% moisture (dotted line) and starch with 25% moisture (dashed line). Starch data are from Willett et al. (16).

Tensile properties of the laminates were also measured using the Instron Testing Machine. Rectangular specimens 75×12.7 mm were cut using a twin blade cutter (Testing Machines, Inc., Amityville, N.Y.). The gauge length was 50.8 mm and crosshead speed was 50 mm/min. Results are the average of tests of 5 specimens.

Thicknesses of the starch and polyester layers were measured by a Precision Micrometer, Model 49-63 (Testing Machines, Inc., Amityville, N.Y.) and a Mini-test 3001 (Elektro-Physik, Cologne, Germany).

X-ray diffraction analysis was performed with a Philips 1820 diffractometer operated at 40 KV, 30 mA with graphite filtered CuK_α radiation and a theta compensating slit. Film samples were mounted on a zero background sample holder. Data were acquired in 0.05 degree two theta, 4 s steps. Percent crystallinities were estimated by the ratio of the area of the crystalline diffraction peaks to the total area under the curves. Areas were measured by cutting and weighing.

Scanning electron microscopy of the laminates was performed with a JEOL JSM-6400V microscope. Samples were mounted on aluminum stubs with graphite filled tape and vacuum coated with gold/palladium.

Melt viscosities of PCL samples were measured using a Brabender PL 2000 extruder and capillary dies essentially as described by Willett *et al.* (16). The extruder was 3/4 inch diameter, 30/1 L/D with a 3/1 compression ratio screw. Dies selected were 2 mm in diameter and had L/D ratios of 20/2, 30/2 and 40/2. The temperatures of three barrel and one die heating zones were all 110°C (except that the first zone for the PCL 767 was set to 50°C). Screw speeds ranged from 5 to 53 rpm. Pressures were measured with a Dynisco transducer prior to the capillary entrance while outputs were measured by weighing the extrudate after 30 s of flow. Procedures for calculation of apparent shear stress and rate and corrections for capillary end effects in the shear stress (Bagley correction) and for shear rate (Rabinowitsch correction) were carried out as described by Rohn (17). Starch melt viscosities at 110°C and 25% and 35% moisture were calculated from the data of Willett *et al.* (16) and interpolation using their Eq 6.

RESULTS

Figure 1 shows melt viscosity data for PCL 767 and 787 as compared to starch plasticized with 25% and 35% water. Over the whole range of shear rates, the viscosity of PCL 787 is larger than the viscosities of the starch while the viscosity of PCL 767 is much lower than starch.

Table 1 shows the effects of varying the melt viscosity of the center starch and outer PCL layers on representative values of the thicknesses of the extruded layers. The viscosity of the starch layer was increased by decreasing water content while the viscosity of the PCL layers was increased by increasing molecular weight. Laminates prepared with low molecular weight PCL (767) were very uniform in terms of both the thicknesses of the starch center layer and the outer PCL layers. Laminates prepared with high molecular weight PCL (787), however, had thick areas of starch in the center of the sheet (viscous fingering) when the starch had a high moisture content and hence low viscosity. It seemed as though the less viscous starch could not "push" its way through the more viscous PCL. Outer, PCL layers were thicker near the edge of sheet. Starch and PCL layers became more uniform in thickness as starch viscosity increased (lower moisture) and feedblock and die temperatures increased. Thicknesses of the polyester coatings generally increased with increasing screw speed, but by less than the factor of 2 expected from the change in screw speed.

Table 2 shows peel strength data for laminates prepared under similar conditions as those in Table 1. Peel strengths were very low for laminates prepared with low molecular weight PCL (767). In most cases, the films spontaneously peeled off the starch after standing for a short time. Peel strengths were much (10–100 times) larger for laminates prepared with high molecular weight PCL (787) and spontaneous delamination seldom occurred. Water content of the starch and coextruder speed did not seem to influence peel strengths significantly.

There is a high degree of variability in peel strength values for PCL 787/starch (compare values for different

Table 1. Effects of Composition and Extrusion Conditions on Laminate Structure.

Water Content in Starch (%)	Outer Layer Polymer	Feedblock, Die Temperatures (°C)	Screw Speed of Coextruder (rpm)	Total Sheet Thickness (mm)		Outer Layer Thickness (μm)	
				center	edge	center	edge
35	PCL 767	115, 80	10	1.8	1.3	7.7	3.5
"	"	"	5	3.2	3.0	2.7	3.0
25	"	"	10	3.6	2.9	3.3	2.9
"	"	"	5	2.6	2.8	2.5	2.3
35	PCL 787	115, 80	5	6.6*	2.3	5.7	26
25	"	"	10	4.4	2.6	15	56
"	"	"	5	6.3	3.1	13	45
25	"	130, 100	10	2.1	1.4		
20	"	145, 110	10	2.2	1.8	10	19

*Center thickness was very irregular because "fingers" of starch/water.

Temperatures of the twin screw and single screw extruders were up to 130°C except for last row (150°C).

Table 2. Effects of Water Content in the Starch Layer and Molecular Weight of the Polymer Coating on Peel Strengths of Starch Based Laminates.

Water Content in Starch Layer During Extrusion (%)	Skin Layer Polymer	Coextruder Speed (rpm)	Peel Strength (N/mm)
35	PCL 767	10	0.002 ± 0.001
"	"	5	0.001
25	"	10	0.001
"	"	5	0.002
35	PCL 787	10	0.018 ± 0.005
"	"	5	0.022
25	"	10	0.020
"	"	5	0.017

Peel strengths were the average of measurements after 7 and 28 days; representative values of the standard deviations are given. Twin screw temperatures were up to 130°C; feedblock and die temperatures were 115 and 80°C, respectively.

runs in Tables 2–4). The reason for this is unknown but may be the changes in processing conditions during and between runs such as variability in feed rates, extruder surging, die pressure and takeoff speed (see below). Differences in drying rate due to polyester coating variations or subsequent shrinkage variations may also be involved.

In order to determine why larger peel strengths were obtained for starch/PCL 787, studies of the film and interface structure by X-ray diffraction and scanning electron microscopy were undertaken. X-ray diffraction patterns (Fig. 2) of PCL films after delamination from the starch indicate that the structures of the PCL 767 and 787 films are similar, with the former and latter having crystallinities of 68% and 63%, respectively. The morphology of the laminates, as revealed by scanning electron micrographs (SEMs) of the surfaces of the starch and PCL after delamination, are given in Fig. 3. The surface of the starch in the starch/PCL 767 laminate is rather smooth while the starch surface from the starch/PCL 787 laminate was variable from smooth with some striations to quite rough. The latter appears to have breaking waves similar to what is commonly observed during interfacial instability in many coextrusions (see **Discussion**). As the interfacial stress increases, the interface changes from smooth to wavy to severe instability with foldover of wave crests (18, 19). The surfaces of the PCL 767 and 787 also appear fairly smooth and rough, respectively. The roughness of the starch/PCL 787 interface probably allows a good mechanical coupling of the starch and PCL layers, thus giving a much larger peel strength. The variability in surface roughness probably accounts for the variability in peel strengths observed.

Table 3 shows the effect of added plasticizer (glycerol/sorbitol) on the peel strengths of starch/PCL 787 laminates. It can be seen that peel strength decreases with added plasticizer, perhaps due to migration of the plasticizer to the starch/PCL interface.

The effect of the type of polyester coating on the peel strengths of starch/polyester laminates is shown in Table 4. The peel strength of a good adhesive (duct tape on steel) is also shown for comparison. Peel

strengths were similar (within experimental error) for the different polyesters except, perhaps, for BAK 1095 and PLA which were difficult to peel off the starch. This suggests that adhesion of these polymers to starch may be greater than the other polyesters. This would not be unexpected since BAK 1095 has a polar amide group, which could hydrogen bond with starch, while PLA has a shorter hydrophobic hydrocarbon segment (and hence is more hydrophilic) than the other polyesters. In addition, PLA and BAK 1095 may tend to interact with starch more since the tendency for self association, as measured by the crystallinity of PLA (0%) and BAK 1095 (33%), is less than that of PCL 787 (63%) and Bionolle 3001 (41%) (20). It should be noted, however, that the difficulty in peeling PLA and BAK films may also be due to the weakness of the film itself. This was especially apparent in the case of PLA, which broke rather easily and may have degraded somewhat during high temperature processing in the presence of water. The BAK polymer was rather soft and also broke fairly easily when peeling

Table 3. Effect of Plasticizer on Peel Strengths of Starch/PCL 787 Laminates.

Starch Layer Composition	Peel Strength (N/mm)
starch/water 75/25	0.06 ± 0.03
starch/sorbitol/glycerol/water 68/8/4/20	0.01 ± 0.01

Feedblock, plate and die temperatures were 105, 95 and 90°C; tested after 2 weeks at 23°C, 50% humidity.

Table 4. Effect of Coating Polymer Type on Peel Strengths of Starch Based Laminates

Polymer	Peel Strength (N/mm)	
	1 week aging	12 weeks' aging
PCL 787	0.02 ± 0.01	0.04 ± 0.02
Bionolle 3001	0.05 ± 0.03	0.08 ± 0.04
Copolyester 14766	0.01 ± 0.01	0.03 ± 0.01
PLA	0.05*	0.04*
BAK 1095	n.d.*	n.d.*
Duct tape on steel	0.18	

*Polymer films were difficult to peel off without breaking film. Coextruder temperature was 170°C. Twin screw temperatures were up to 130°C; feedblock and die temperatures were 135 and 105°C, respectively.

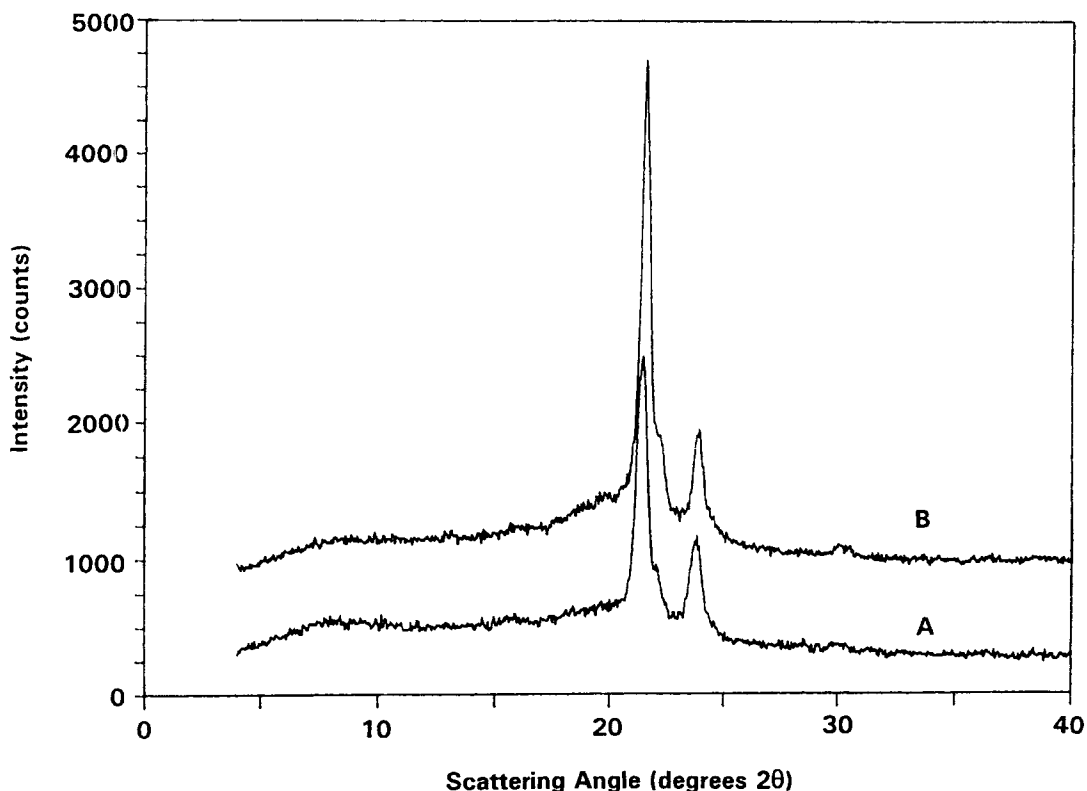


Fig. 2. X-ray diffraction scans of PCL films after delamination from starch. PCL 767 (A) and PCL 787 (B).

was begun. Experiments were attempted to laminate a strong, adhesive layer over the polyester such as duct tape or Bytac and then peel, but the PLA and BAK coatings remained adherent. Dipping the sample end in water to try and delaminate the polyester did not seem to help.

The effect of type of polyester coating on the mechanical properties of the laminates is shown in Table 5. Measurements were made after 3 months' aging at 50% humidity so the moisture content of the starch should have reached equilibrium. There was no significant difference in the tensile strength, elongation to break or modulus of elasticity of the starch sheets laminated with different polyesters. The values, moreover, are similar to those for extruded starch sheets alone (21). This is not surprising since the coatings constitute only a small (~2) percentage of the total weight of the laminate.

DISCUSSION

The study of layer uniformity and interfacial instability in multilayer coextrusion has been the subject of many experimental and theoretical investigations (18, 19, 22–34). It is apparent from these studies that an overall understanding of the observed phenomena has not yet been achieved. Nevertheless, there are certain guiding principles that can be used to interpret our experiments and suggest ways to increase or decrease the uniformity or interfacial instability in starch/polyester systems.

It is often found in bilayer coextrusions, for example, that the less viscous layer will partially surround the more viscous layer, thus reducing the shear stress at the wall and the total energy (19, 26, 28). This is consistent with the observation that the low viscosity PCL 767 uniformly coats the inner, higher viscosity starch layer. One might expect the PCL layer near the edge of the sheet to be thicker than the center due to encapsulation of the starch but this was only observed in some experiments.

For the case in which PCL 787 is the outer layer, the less viscous starch inner layer is encapsulated by the higher viscosity 787, in apparent contradiction to the above. Khomami and Ranjbaran (27) have also observed similar behavior for encapsulation of a low viscosity polyethylene by a higher viscosity polypropylene. They attributed this to first and second normal stress differences of the polymers based on experimentally observed flow velocities. Similarly, Dooley *et al.* (32, 33) found significant secondary flows normal to the main flow direction that distorted the layered structure. They were able to reproduce the experimental behavior using a viscoelastic model that incorporated a non-zero second normal stress difference. It may be that a relatively narrow "finger" of starch encapsulated within PCL 787 has a lower energy since less work is required to pull apart the elastic 787 in this configuration than in wider layers. Note also that the layers of the extrudates are more uniform in thickness at high feedblock and die temperatures likely

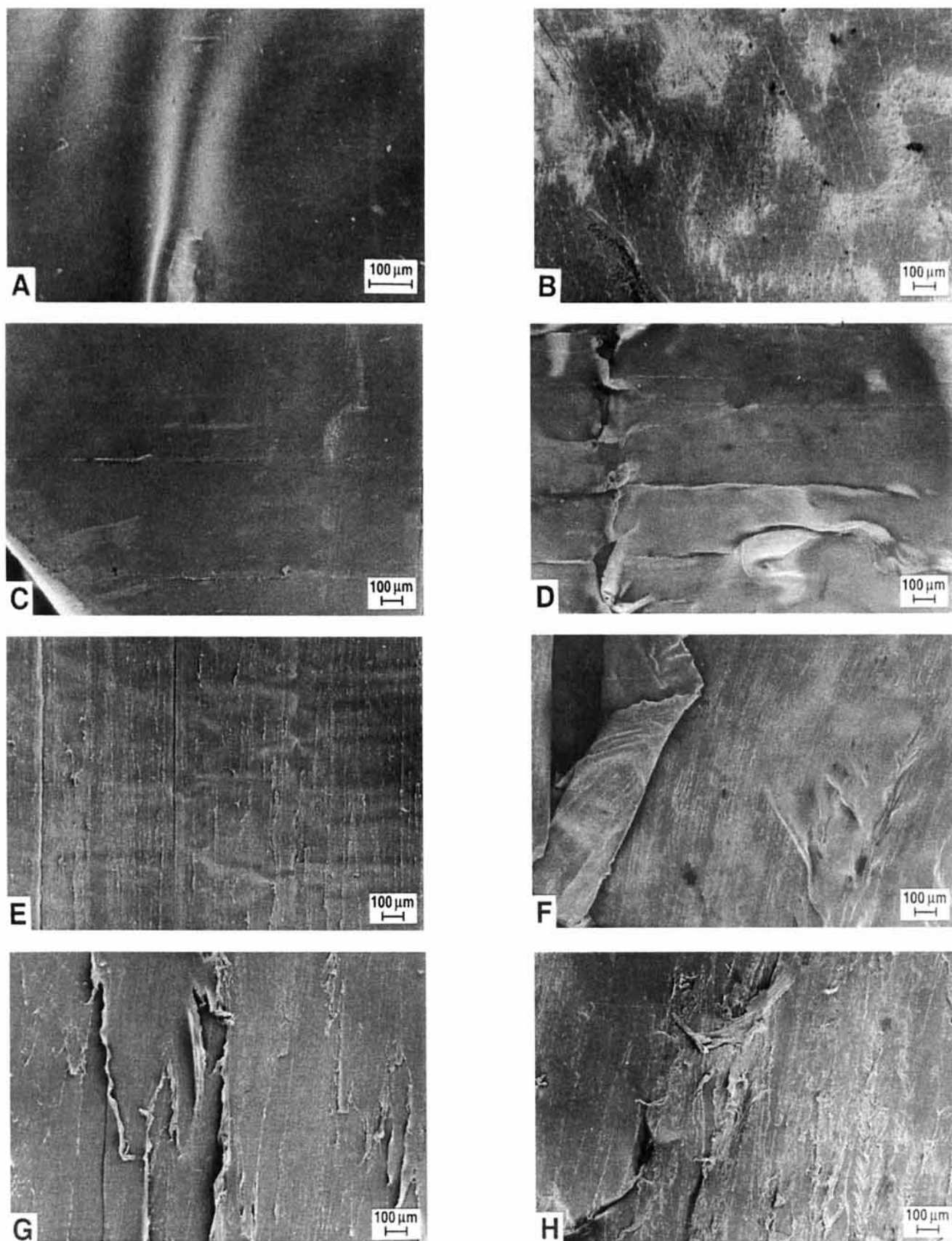


Fig. 3. Scanning electron micrographs of starch and PCL surfaces after delamination: starch/PCL 767: starch (A), PCL (B); starch/PCL 787: starch (C, E, G), PCL (D, F, H).

Table 5. Effect of Coating Polymer Type on Tensile Properties of Starch Based Laminates*.

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)
PCL 787	44 \pm 5	7.8 \pm 4.9	2.0 \pm 0.2
Bionolle 3001	41 \pm 6	6.1 \pm 1.9	2.0 \pm 0.2
Copolyester 14766	40 \pm 6	8.1 \pm 3.9	2.1 \pm 0.2
PLA	38 \pm 4	6.4 \pm 2.4	1.8 \pm 0.2
BAK 1095	42 \pm 6	7.0 \pm 4.0	2.0 \pm 0.2

*Tests were conducted after 12 weeks' aging at 23°C, 50% relative humidity. Results for samples made at 5 and 10 rpm coextruder speeds were the same within experimental error and were averaged together. Coextruder temperature was 170°C. Feedblock and die temperatures were 135 and 105°C.

because of the decrease in elasticity of the PCL. Thus, the elastic properties of PCL 787 may be a crucial determinant of the thicknesses of starch and PCL layers.

Interfacial instabilities in coextruded multilayer sheets manifest themselves as waves and striations in the interface (25). They are normally considered detrimental in plastics applications since they cause haze in an otherwise clear material. Instabilities are thought to arise when the interfacial shear stress exceeds a certain critical level (18, 19, 22, 25). This can happen when different polymers in the different layers have different melt viscosities (22, 25) or elasticities (23, 29, 31). Instabilities can arise even with two layers of the same polymer melt when the layers have different flow rates (34). In addition, factors such as layer thickness, die design and upstream pressure variations have been found to influence whether instabilities form (19, 24, 26).

Instabilities were absent for starch/PCL 767 laminates possibly because the shear stress transmitted through the low viscosity 767 from the wall to the interface would be expected to be low. Similarly, Khomami and Ranjbaran (27) found no instabilities for 3-layer extrudates in which low viscosity HDPE formed the outer layers and a high viscosity PP was the inner layer, as long as the thickness ratio of HDPE/PP was below 0.60. They suggested that the thin, less viscous outer layers damped out longwave disturbances while the more elastic center layer stabilized intermediate and shortwave disturbances. (In their experiments, periodic pressure pulses were generated by thrusting of one of the extruder screws.) On the other hand, when the more viscous and elastic PP made up the thinner, outer layer, interfacial instabilities were seen. Our observation of a wavy interface for the case of PCL 787/starch is consistent with these results.

Clearly, our data indicate that interfacial instabilities between the starch and PCL layers give rise to much better interfacial bonding. There are several possible ways of controlling or augmenting the instability and hence improving the bonding. These include increasing the interfacial shear stress by increasing flow rates, reducing die temperatures, making the outer layer thinner, reducing the die gap or lengthening the die (24). Mavridis and Shroff have (29) demonstrated that these changes do indeed reduce the clarity of trilayer films as well as increase the interfacial shear stress as calculated from viscoelastic data and flow equations. Since viscoelastic data are, at present,

unavailable for starch (owing to difficulties in retaining water during high temperature measurements), it would be difficult to calculate flow fields in multilayer coextrusions of starch and polyesters.

Previous work on the adhesion of solution cast polyester films to smooth starch/polyvinyl alcohol films showed very low peel strengths (<0.003 N/mm) (35), similar to those obtained here for PCL 767. This was rationalized in terms of the high interfacial tension between the very hydrophilic starch and the rather hydrophobic polyesters (35). Higher peel strengths (0.10 N/mm) were obtained for PCL films cast onto starch foams (35) that have a rougher surface and thus better mechanical interlocking. Similar to our results, Lawton (35) reported peel strengths that were higher for PLA than PCL and correlated this with the observation of the surface free energy of PLA being closest to starch. It should be noted that adhesion of polymers is also affected by their viscoelastic properties such that adhesive strength is inversely proportional to G' (at the bonding frequency, temperature) and proportional to G'' (at debonding frequency, temperature) (36). These parameters will obviously be different for different coating polymers. Interfacial bonding has been improved by modifying the surface of the starch by, for example, solvent swelling (37), corona discharge (37) or by coating with a natural resin having a solubility parameter intermediate between starch and polyesters (38). Poly(hydroxyester-ethers) have also been shown to act as an effective tie layers between starch and polyesters, showing good adhesion to both polymers (39). Tie layers could certainly be added to increase the adhesion of starch and polyesters during coextrusion, although the adhesion achieved simply by manipulation of interfacial instability may be adequate for many uses.

The main goal of this work was to assess the feasibility of preparing water resistant starch sheets by coextrusion techniques. Previous studies of the water vapor permeability of biodegradable polyesters showed that thin polyester coatings have sufficient water resistance to protect starch sheets from water for a limited time (hours-days) (20). This was qualitatively confirmed in the present work by placing drops of water or aqueous solutions of I_2/KI on the laminated starch sheets and observing the time required for underlying softness or blue color to develop (data not shown). In general, the sheets showed uniform water resistance (few pinholes or cracks) with hours required to observe significant water penetration.

Delamination of the polyester films underneath the water droplets did not seem to occur readily.

Although tensile strengths and breaking strains of polyester laminated starch sheets measured at 50% humidity (Table 5) are fairly good, decreased strength and elongation become a significant problem for thermoplastic starch at lower humidities because of loss of plasticizing water (21). Some possible ways to lessen this problem include adding polymeric plasticizers such as polyvinyl alcohol (40), using starches having a larger fraction of the linear (amylose-like) component (21) and chemically modifying starch to "internally" plasticize the molecule (41). Foaming the starch using water as a blowing agent during extrusion also seems to introduce flexibility into the overall sheet structure (42).

Several different type of products might be produced by the multilayer coextrusion of thermoplastic starch compositions with polyesters. Polyester/starch foam/ polyester sheets prepared by coextrusion followed by thermoforming into shaped objects such as plates and clamshells may well be feasible and functional commercially. Flexible blown films comprising a starch/PVOH inner layer and thin, outer polyester layers may be useful in applications such as biodegradable compost bags or agricultural mulch film. Laminates might also be useful for controlled release of agricultural chemicals and biopesticides or for the enclosure of diet formulations for raising insects beneficial to crops.

In summary, 3-layer sheets containing a thermoplastic starch inner layer and thin, polyester outer layers were prepared by coextrusion. The application of a thin coating gave adequate water resistance over short periods (hours) with a relatively small added materials cost over that for starch alone. Laminates made with high molecular weight polyester coatings had much higher peel strengths than those made with lower molecular weight polyesters, probably because of greater surface roughness in the former. More research is needed in the area of additives to the starch phase to improve flexibility and in the characterization of the viscoelastic properties of thermoplastic starch to predict flow patterns. More work is also needed to develop methods to prepare laminated starch foams and films.

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